JAPANESE / ENGLISH TRANSLATION OF

Source: Japanese Patent Application JP 2 – 38445 A

Title of the Invention: Polyester Resin Composition

Your Ref: No. 2406

For: Eastman Chemical Company - Library and Information Services (LibrIS)

(54) Title of the Invention: **Polyester Resin Composition**

(72) Inventor: Hiroo Karasawa
c/o Toray Industries, Inc.
9-1 Oe-cho, Minato-ku
Nagoya-shi, Aichi-ken

(72) Inventor: Kiichi Yonetani
(Same as above)

(72) Inventor: Seiichi Nakamura
(Same as above)

(71) Applicant: Toray Industries, Inc.
2-2-1 Nihonbashi Muromachi
Chuo-ku, Tokyo

SPECIFICATION

1. Title of the Invention

Polyester Resin Composition

2. Claims

A polyester resin composition formed as a result of adding 0.005 to 10 parts by weight of malonic acid ester or β-ketoester, and/or a metal chelate thereof, per 100 parts by weight of thermoplastic polyester.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a polyester resin composition in which the crystallization velocity is high, the mold release characteristics of a molded article are excellent when a low-temperature mold is used, gas generation is minimal, and the mechanical properties are good.

(Prior Art)

Injection molding is a technique that is rapidly being applied in a greater number of fields in recent years due to the fact that three-dimensional molded articles can be obtained from resin in a simple manner and at low cost. The applied resins for injection molding are spreading from polyethylene, polypropylene, and other general-use resins to nylon, PBT, POM, and other engineering plastics, as well as PPS, PES, and other special purpose resins.

Recently, polyethylene terephthalate, polycyclohexane dimethylene terephthalate, polyethylene naphthalate, and the like are rapidly receiving attention as materials for injection molding due to their high heat resistance.

Nevertheless, since polyester has a low crystallization velocity, there are drawbacks in that the molding cycle is long, the mold temperature must be set high, and other problems occur, and it is known to be a resin that is difficult to apply in injection molding.

In order to resolve such difficulties, methods have been proposed whereby talc and other inorganic material; the higher fatty acid salts disclosed in JP (Kokai) Nos. 55-52340, 55-60552, and other publications; the acetylacetone metal salts disclosed in JP (Kokai) Nos. 56-41247, 57-14644, and other publications; the alkaline metal salts of dehydroacetic acid disclosed in JP (Kokai) 63-15840; and other substances are added as crystallinity improvers.

(Problems to Be Solved by the Invention)

However, the crystallization velocity of polyester is not significantly improved as a result of these methods, and they present additional drawbacks in that large quantities of gas are produced during molding, and the mechanical characteristics also tend to be compromised.

Therefore, an issue in the industry is to improve the moldability of polyester without generating gas and reducing the mechanical characteristics.

(Means Used to Solve the Above-Mentioned Problems)

In view of the above, the present inventors, as a result of thoroughgoing research aimed at obtaining a crystallinity improver in which the crystallization velocity of polyester is markedly improved and the generation of gas during molding is low, arrived at the present invention having discovered that the above-described drawbacks are solved when a malonic acid ester, a β-ketoester, and/or a metal chelate thereof are added to polyester.

More specifically, the present invention provides a polyester resin composition formed as a result of adding 0.005 to 10 parts by weight of malonic acid ester or β-ketoester, and/or a metal chelate thereof, per 100 parts by weight of thermoplastic polyester.

The thermoplastic polyester used in the present invention is a polymer or copolymer obtained as a result of a polycondensation reaction in which the main components are a dicarboxylic acid (or an ester-forming derivative thereof) and a diol (or an ester-forming derivative thereof).

Examples of the dicarboxylic acid used herein include terephthalic acid, isophthalic acid, orthophthalic acid, 1,5-naphthalene dicarboxylic acid, 2,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,2'-biphenyl dicarboxylic acid, 3,3'-biphenyl dicarboxylic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-biphenylether dicarboxylic acid, 4,4'-diphenylmethane dicarboxylic acid, 4,4'-diphenylsulfone dicarboxylic acid, 4,4'-diphenyl isopropylidene dicarboxylic acid, 1,2-bis(phenoxy) ethane-4,4'-dicarboxylic acid, 2,5-anthracene dicarboxylic acid, 2,6-anthracene dicarboxylic acid, 4,4'-p-terphenylene dicarboxylic acid, and 2,5-pyridine dicarboxylic acid; and preferable among these are terephthalic acid and 2,6-naphthalene dicarboxylic acid.

Two or more of these dicarboxylic acids may be mixed and used together. It should be noted that in addition to these dicarboxylic acids, one or more of the following may be mixed and used in small amounts: aliphatic dicarboxylic acids such as adipic acid, azelaic acid, dodecanedioic acid, and sebacic acid; and cycloaliphatic dicarboxylic acids such as cyclohexane dicarboxylic acid.
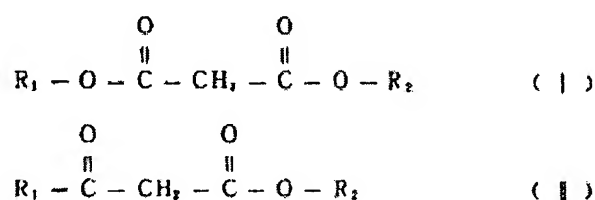
Examples of the diol component include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, neopentyl glycol, 2-methyl-1,3-propane diol, diethylene glycol, triethylene glycol, and other aliphatic diols; 1,4-cyclohexane dimethanol and other cycloaliphatic diols; and mixtures thereof. One or more of the following with a molecular weight of 400 to

6,000 may be copolymerized as long as they are used in a small amount: polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and other long-chain diols.

Specific examples of the polyester include polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polycyclohexane dimethylene terephthalate, polyethylene naphthalate, polybutylene naphthalate, and polyethylene-1,2-bis(phenoxy) ethane-4,4'-dicarboxylate, as well as copolyesters such as polyethylene isophthalate/terephthalate, polybutylene terephthalate/isophthalate, and polybutylene terephthalate/decane dicarboxylate. Preferred among these are polybutylene terephthalate, polycyclohexane dimethylene terephthalate, polyethylene naphthalate, and polyethylene terephthalate, which have a good balance between mechanical properties and moldability.

The polyester used in the present invention has an intrinsic viscosity of 0.25 to 3.0 dL/g, and preferably 0.4 to 2.25 dL/g, when measured at a temperature of 25°C in an o-chlorophenol solution.

The malonic acid esters or β-ketoesters used in the present invention are those that have the structural units of the following general formula (I) or (II).

$$R_1 - O - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - O - R_2 \qquad (I)$$

$$R_1 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - O - R_2 \qquad (II)$$

(In the formulas, R_1 and R_2 are alkyl groups, aromatic groups, or aliphatic-alicyclic groups. R_1 and R_2 may bond together to form a ring structure.

It should be noted that the chemical structure of the malonic acid esters and β-ketoesters is always referred to in the present invention as a keto structure, but the structure may also be a compound described as a corresponding ethanol structure.
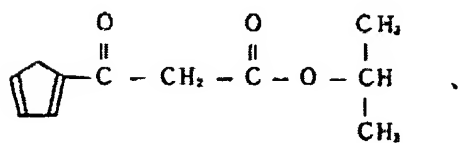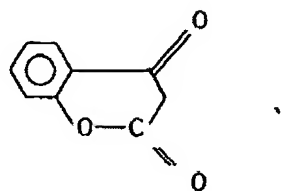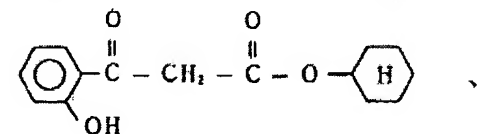
Specific examples of R_1 and R_2 in general formulas (I) and (II) include methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, dodecyl, octadecyl, benzyl, cyclohexyl, cyclohexylmethyl, and other alkyl groups; and phenyl, naphthyl, methylphenyl, chlorophenyl, hydroxyphenyl, and other aromatic groups. Examples of groups when R_1 and R_2 bond to form a ring structure include trimethylene, tetramethylene, and pentamethylene.

Specific examples of the malonic acid ester of general formula (I) include dimethyl malonate, diethyl malonate, diisopropyl malonate, di-t-butyl malonate, didodecyl malonate,

dioctadecyl malonate, dibenzyl malonate, diphenyl malonate, dinaphthyl malonate, and dicyclohexyl malonate. Preferred are diisopropyl malonate, di-t-butyl malonate, dicyclohexyl malonate, and other esters of malonic acid with secondary or tertiary alcohols, and most preferred are cases in which the molecular weight of the malonic acid ester is 150 or more.

Of the β-ketoesters expressed with the help of the general formula (II), preferred are those that have an unsaturated bond that conjugates with the carbonyl carbon, and they preferably have an aromatic group. The ester mo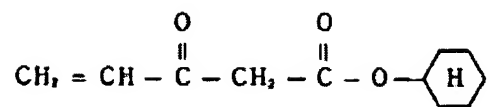iety is preferably an ester from a secondary or tertiary alcohol in the same manner as a malonic acid ester, and the molecular weight of the β-ketoester is most preferably 150 or more.

Preferred examples of the compounds expressed with the help of the general formula (II) include those shown below:

$$
\text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-t-Bu \quad ,
$$

$$
(Cl)\text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-t-Bu \quad ,
$$

$$
\text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{CH}} \quad ,
$$

$$
\text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\langle H \rangle \quad ,
$$

$$
(OH)\text{Ph}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\langle H \rangle \quad ,
$$

(cyclic structure) ,

$$
\text{(cyclopentadienyl)}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{CH}} \quad ,
$$

and

$$CH_2 = CH - \overset{\overset{O}{\|}}{C} - CH_2 - \overset{\overset{O}{\|}}{C} - O - \langle H \rangle$$
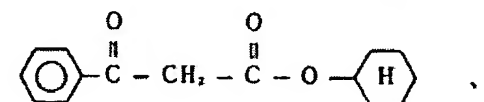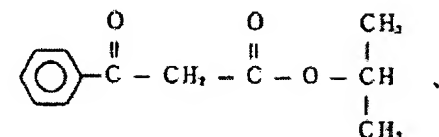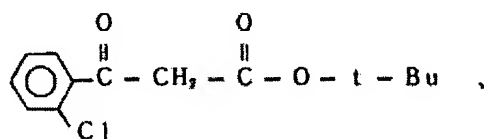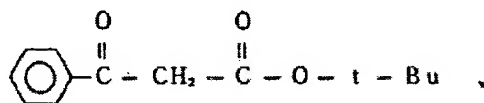
Examples of the metals in the metal chelates of the malonic acid esters or the β-ketoesters of the present invention include lithium, sodium, potassium, cesium, rubidium, and other alkali metals; barium, strontium, calcium, magnesium, and other alkaline-earth metals; and titanium, iron, and the like. Among these, sodium, potassium, and lithium are preferred.

In the present invention, the malonic acid ester, or the β-ketoester and/or metal chelate thereof may be used alone, or two or more types may be used together.

The addition amount of the β-ketoester of the present invention, and/or metal chelate thereof, is 0.005 to 10 parts by weight, is preferably 0.01 to 5 parts by weight, and is more preferably 0.05 to 5 parts by weight, per 100 parts by weight of the thermoplastic polyester. If the addition amount is less than 0.005 parts by weight, the effect of improving the crystallinity of the polyester is not sufficient, and if the addition amount exceeds 10 parts by weight, the molecular weight of the polyester during manufacture of the thermoplastic polyester resin composition decreases, and the dynamic properties of the molded article tend to be compromised, and both cases are accordingly not preferred.

From the viewpoint of improving moldability, the composition of the present invention is preferably jointly used as required with organic acid salts or inorganic compounds. Specific examples of such compounds include sodium stearate, barium stearate, sodium salts or barium salts of partially saponified montanic acid esters, ionomers, sodium salts of phenols such as nitrophenol and formyl phenol, and talc.

Furthermore, the moldability can be further improved with the help of a method in which a compound known as a crystallization promoter and used in thermoplastic polyesters such as polyethylene terephthalate is added to the composition of the present invention. Specific examples of such crystallization promoters include polyethylene glycol, polypropylene glycol, and other polyalkylene glycols or carboxylic acid diesters thereof; α,ω-dialkyl etherified polyethylene glycols, α,ω-dialkyl etherified polypropylene glycols, and other α,ω-dialkyl etherified polypropylene glycols; neopentyl glycol dibenzoate and other benzoic acid esters; and polylactone, polyethylene adipate, and other aliphatic polyesters.

It should be noted that as a result of further adding fibrous and/or granular fillers to the composition of the present invention, the rigidity can be considerably improved without compromising other physical properties, although this is not essential. Examples of such fillers include glass fibers, carbon fibers, metal fibers, aramid fibers, asbestos, potassium titanate whiskers, wollastonite, glass flakes, glass beads, talc, mica, clay, calcium carbonate, barium sulfate, titanium oxide, and aluminum oxide. Preferably used among these are chopped strand types of glass fiber, talc, and titanium oxide. The amount of the fillers added is ordinarily equal to or less than 120 parts by weight per 100 parts by weight of the polyesters.

One or more of ordinary additives such as antioxidants, thermostabilizers, UV absorbers, lubricants, mold release agents, and colorants, including dyes and pigments, may be added to the composition of the present invention in a range that does not compromise the object of the present invention.

A small amount of thermoplastic resin (examples of which include polycarbonate, polyphenylene ether, polyamide, polypropylene, polyethylene, ionomer, ethylene/propylene copolymer, ethylene/butene-1 copolymer, ethylene/propylene/non-conjugated diene copolymer, ethylene/ethyl acrylate copolymer, ethylene/glycidyl methacrylate copolymer, ethylene/vinyl acetate/glycidyl methacrylate copolymer, and ethylene/propylene-g-maleic anhydride copolymer) may also be added.
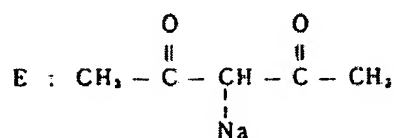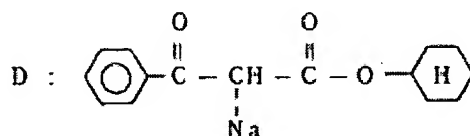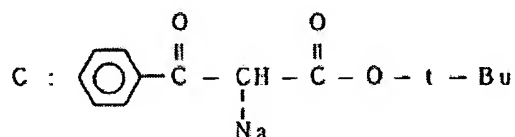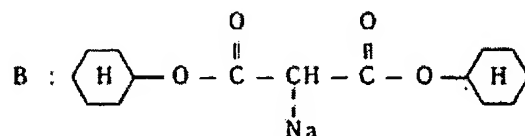
The method of producing the composition of the present invention is not particularly limited, but examples of preferably used methods include a method in which both a polyester and a malonic acid ester or β-ketoester, and/or a metal chelate thereof, are melted and mixed using an extruder, and a method for adding a malonic acid ester or a β-ketoester, or a metal chelate thereof, in the final stage of polymerization of the polyester. When inorganic filler or another additive is added, the additive is preferably melted and blended in at the same time as the two components described above using an extruder.

The resin composition of the present invention can easily be molded by means of injection molding, extrusion molding, or another ordinary method, and the resulting molded article has high crystallinity and exhibits excellent properties.

The effect of the present invention is described in greater detail with working examples below. The intrinsic viscosities in t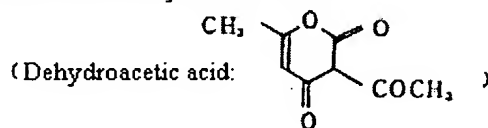he examples are values measured in an o-chlorophenol solution at 25°C, and the parts and percentages are both based on weight.

Working Examples 1 to 6 and Comparative Examples 1 to 5

Additives (A) to (F) described below were blended in the ratios shown in Table 1 based on 100 parts by weight of polyethylene terephthalate (PET) with an intrinsic viscosity of 0.83 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 280°C.

$$A: \quad t-Bu-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{Na}{|}}{CH}-\underset{\underset{O}{\|}}{C}-O-t-Bu$$

$$B: \quad \langle H \rangle-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{Na}{|}}{CH}-\underset{\underset{O}{\|}}{C}-O-\langle H \rangle$$

$$C: \quad \langle O \rangle-\underset{\underset{O}{\|}}{C}-\underset{\underset{Na}{|}}{CH}-\underset{\underset{O}{\|}}{C}-O-t-Bu$$

$$D: \quad \langle O \rangle-\underset{\underset{O}{\|}}{C}-\underset{\underset{Na}{|}}{CH}-\underset{\underset{O}{\|}}{C}-O-\langle H \rangle$$

$$E: \quad CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{Na}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$
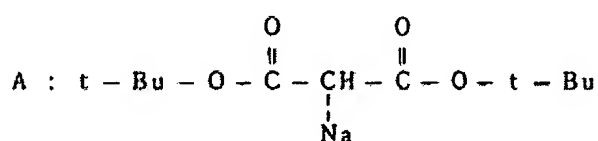
F: Sodium salt of dehydroacetic acid

(Dehydroacetic acid: CH_3 — ring structure — $COCH_3$)

The resulting polyethylene terephthalate composition was subjected to differential thermal analysis using a differential scanning calorimeter, the heating crystallization temperature and cooling crystallization temperature were measured, and crystallinity was evaluated. It is generally well known that crystallinity is improved as the cooling crystallization temperature

increases and as the heating crystallization temperature decreases, so ΔT (defined as $\Delta T =$ (Cooling crystallization temperature) – (Heating crystallization temperature)) was therefore used as a measure for the crystallinity.

Next, weight reduction was measured using a differential thermogravimeter when the pellets were left standing for one hour at a temperature of 290°C in nitrogen, and the result was used as a measure of the amount of gas released during molding.

The results are shown in Table 1.

It is apparent from the results of Table 1 that the composition of the present invention is formed such that ΔT is considerable, the crystallization characteristics are markedly improved, and the generation of gas is minimal.

Working Example 7 and Comparative Example 6

Additive (A) was blended in the ratio shown in Table 1 based on 100 parts by weight of polycyclohexane dimethylene terephthalate (PCT) with an intrinsic viscosity of 0.94 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 305°C.

Next, weight reduction was measured using a differential thermogravimeter when the pellets were left standing for one hour at a temperature of 310°C in nitrogen, and the result was used as a measure of the amount of gas released during molding. The example (comparative example 6) in which the additive (A) was not added was measured in the same manner.

The results are shown in Table 1.

Working Examples 8 to 10 and Comparative Examples 7 to 10

Additives (A) to (F), and 50 parts of chopped-strand glass fiber (length: 3 mm, diameter: 11 μ) were blended in the ratios shown in Table 2 based on 100 parts by weight of polyethylene terephthalate with an intrinsic viscosity of 0.61 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 280°C.

The resulting polyethylene terephthalate composition was subjected to differential calorimetry and differential gravimetry in the same manner as described in working example 1.

Table 1

Example			Nucleating agent		ΔT (°C) *1	Thermal reduction (%) *2	Base polymer
		Type	Added amount (parts)				
Working Example	1	A	0.5		85	0.90	PET
	2	B	0.5		87	0.92	PET
	3	C	0.5		92	1.0	PET
	4	D	0.1		80	0.85	PET
	5	D	0.5		86	0.93	PET
	6	D	2.0		102	1.2	PET
	7	D	0.5		96	1.1	PCT
Comparative Examples	1	-	-		60	0.85	PET
	2	D	0.001		62	1.5	PET
	3	E	0.1		74	2.4	PET
	4	E	0.5		76	3.9	PET
	5	F	0.5		69	2.9	PET
	6	-	-		69	0.91	PCT

*1: The quality of the crystals improves as the value of ΔT increases.
*2: Thermal reduction: The generation of gas is lower as the value decreases.

The pellets were dried at 155°C for 5 hours in a vacuum, and boxlike molded articles were thereafter molded with a length of 45 mm, a width of 65 mm, a depth of 20 mm, and a wall thickness of 2 mm by using a screw inline-type injection molding machine set to a temperature of 275°C, a mold clamping pressure of 75 tons, an injection time of 15 seconds, a cooling time of 20 seconds, an intermediate time of 5 seconds, and a mold temperature of 90°C. The force (mold release force) required to release the molded article from the mold was then determined. Also, under the same injection molding conditions as described above, an ASTM-No. 1 dumbbell was molded, and the tensile characteristics were measured in accordance with ASTM D-638.

The results are shown in Table 2.

Table 2

Example		Nucleating agent		ΔT (°C)	Thermal reduction (%)	Mold release force (kg f) *1	Tensile strength (kg/cm²)	Breaking elongation (%)
		Type	Weight (parts)					
Working Examples	8	A	0.5	95	1.4	56	1540	3.4
	9	B	0.5	97	1.2	60	1590	3.3
	10	C	0.5	96	1.5	69	1550	3.2
	11	D	0.5	95	1.3	58	1560	3.3
Comparative Examples	7	-	-	63	0.92	> 200	1210	3.3
	8	D	0.001	65	1.0	> 200	1250	3.3
	9	E	0.5	69	2.6	> 200	1290	2.0
	10	F	0.5	72	3.2	190	1270	1.9

*1: The mold release characteristics improve as the value of the mold release force decreases.

It is apparent from the results of Table 2 that the composition of the present invention considerably improves the crystallization characteristics even when glass fibers are present, and exhibits excellent mold release characteristics even in a low-temperature mold. It is furthermore apparent that the generation of gas is very minimal and the physical characteristics are good.

(Effect of the Invention)

Since the polyester resin composition of the present invention has good crystallization characteristics, moldability is excellent in a low-temperature mold, the generation of gas is low, and productivity is good; and since the resulting molded article has excellent mechanical properties, the composition can be used as electrical and electronics components, automotive components, mechanical components, and other parts.

Applicant: Toray Industries, Inc.